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New Trinuclear Aquo Ions of Molybdenum

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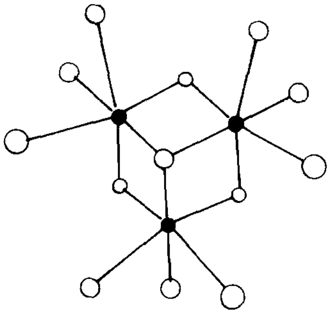
We wish to report experiments in which reversible electrolytic reduction of the aquo Mo(IV)$_3$ ion in acidic solutions yields first the orange-pink Mo(III, III,IV), and then the green Mo(III)$_3$ aquo ion. The latter is also obtained by reduction of Mo(IV)$_3$ with Zn/Hg.

It has now been established that the Mo(IV) aquo ion is a *triangulo* trinuclear species having an $Mo_3O_4^{4+}$ core structure, with three water molecules coordinated to each molybdenum.



X-ray crystal structures of $[Mo_3O_4(C_2O_4)_3(H_2O)_3]^{2-}$, $[(Mo_3O_4)_2(edta)_3]^{4-}$ [3]** and $[Mo_3O_4(NCS)_8(H_2O)]^{4-}$, [4] together with studies using oxygen-18 labelled solvent water [1], have confirmed that the $Mo_3O_4^{4+}$ core present in crystalline samples is retained in solution. Attempts to generate monomeric and dimeric Mo(IV) aquo ions as stable species by oxidation of monomeric [5, 6] and dimeric [7] aquo Mo(III) have proved unsuccessful [8], both oxidations yielding the Mo(V) aquo dimer, $Mo_2O_4^{2+}$, as final product even when there is a stoichiometric deficiency of oxidant.

It has been noted that trinuclear clusters of early transition-metal elements have both a pronounced tendency to form and high stability [9]. Attention has been drawn to the fact that the number of metal-atom valence electrons (*n*) in such clusters is approximately equal to the number required to form single bonds between adjacent pairs of metal atoms.

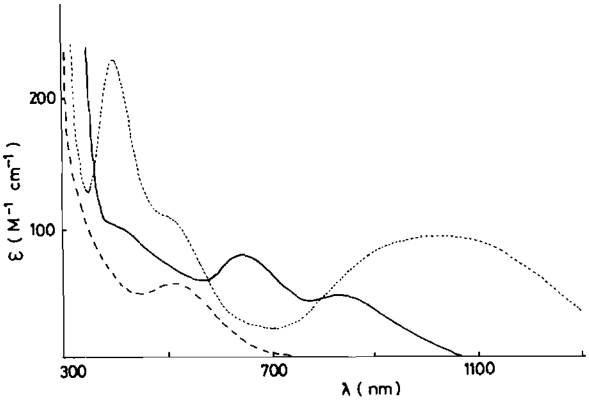


Fig. 1. Spectra of aquo ions Mo(IV)$_3$ (– – –), Mo(III, III, IV) (· · · · ·) and Mo(III)$_3$ (——) in 0.5–4.0 *M* HPTS. Absorption coefficients are per Mo atom. The spectrum of Mo(III,III,IV) was deduced after allowing for Mo(IV)$_3$ and Mo(III)$_3$.

Thus, in terms of a formal shorthand, the clusters may be represented as M_3^n, where n = 6–8 is fairly common, but n = 9 is rare [9].

We wish to report here studies in which the Mo(IV)$_3$ aquo ion (n = 6) in 0.5–4.0 *M* *p*-toluenesulphonic acid, HPTS (a strong redox inactive acid with poor donor properties), is reduced to give a related complex n = 9. Under air-free conditions reduction with amalgamated Zn shot gives a green product which titrates for Mo(III). The spectrum, Fig. 1, is different from that of the green aquo dimer, Mo(III)$_2$, peak positions, nm (ε, M^{-1} cm^{-1}) at 360 (450), 572 (48) and 624 (55) [7, 8]†. The new ion is readily and quantitatively reoxidised to Mo(IV)$_3$, suggesting a closely related trinuclear structure. On allowing access of O_2 an intermediate is observed prior to reformation of Mo(IV)$_3$, spectrum, Fig. 1. Isosbestic points for the first stage are observed at 378, 573 and 810 nm, and titration of solutions exhibiting the full intensity peak of the intermediate at 400 nm (ε 230 M^{-1} cm^{-1}), indicate an average oxidation state of 3.3.

At [H$^+$] > *ca.* 2.0 *M* electrolytic reduction of Mo(IV)$_3$ at a potential of –0.25 V (*vs.* N.H.E.) confirmed these results with evidence for the same Mo(III,III,IV) (n = 8) intermediate, but no evidence for Mo(III,IV,IV). Due presumably to variations in relevant reduction potentials with [H$^+$], <30% of the Mo(III,III,IV) intermediate is obtained at [H$^+$] < *ca.* 0.50 *M*. Rapid equilibration

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**edta ≡ ethylenediaminetetraacetate.

†All absorption coefficients are per Mo atom.

$t_{1/2} < 1$ min) of Mo(III)$_3$ with Mo(IV)$_3$ (2:1 amounts) gives quantitative formation of Mo(III,III,IV) in 4.0 *M* HPTS, 80% in 2.0 *M* HPTS, and 30% in 0.5 *M* HPTS.

The spectrum of Mo(III,III,IV) is identical to that reported by Chalilpoyil and Anson [10], and incorrectly assigned by them as Mo(III)$_2$ dimeric species at a time when there was considerable confusion as to the nature and structure of the Mo(IV) aquo ion. The colour of the Mo(III,III,IV) ion is orange-pink. A feature of the Mo(III,III,IV) spectrum is the intervalence band at 1050 nm which has a small absorption coefficient (ϵ *100* M^{-1} cm^{-1}), to be compared with similar values observed for several dimeric ruthenium complexes in which extensive localisation of oxidation states is indicated [11]. A mixed oxidation state Mo(III,III,IV,IV) complex with edta as a ligand has been prepared previously [12]. From the crystal structure determination all four molybdenums are in equivalent sites [13], and absorption coefficients in the visible range at least are much more intense. These observations are consistent with extensive electron delocalisation.

Cadiot and Lamache [14] have previously reported experiments in which they reduced the Mo(IV) aquo ion polarographically in HCl (and H_2SO_4) 2–6 *M*, and observed uptake of 2/3 and then 1/3 of an electron per Mo. Anionic complexes are present at high acid concentrations, and the Mo(III) product could not be reoxidised. Surprisingly this significant work did not lead to the conclusion that trimers were present [15].

The green Mo(III)$_3$ aquo ion is more strongly held on a Dowex 50-X2 ion-exchange resin than is Mo(IV)$_3$ which suggests that the charge is >4. It is concluded that protonation of oxo bridging ligands occurs on reduction. The rapidity of redox interchanges and fact that isosbestics are retained strongly suggests closely related *triangulo* structures. Single crystal X-ray diffraction studies of the two new aquo ions reported here (or of related complexes) are of considerable interest. As yet no suitable crystals have been obtained.

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